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DETERMINATION OF THE GLASS TRANSITION TEMPERATURE OF A PLASTIC MATERIAL FROM THE VARIATIONS IN ITS PENDULAR HARDNESS

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Bernard Persoz and Geneviève Grenier

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A definition of the glass transition temperature, based on the variation of the pendular hardness (Persoz method) during the transition from the glass-like state to the rubber-like state, is given. The data are applied to four polymers (polystyrenes), and a comparison with other experimental data on the same materials is given. A simple and cheap hardness tester machine is described with which the Brewster coefficient of synthetic resins and other materials can be determined immediately after application of the load.

I. THE PENDULUM USED

Hardness is a rather complex characteristic so that its definition, in the final analysis, is entirely dependent on the reference method used. Among these methods, one is especially simple; this method consists in having a pendulum oscillate on the surface to be studied and measuring the damping or, occasionally, the period of this pendulum.

The originator of such a method apparently was Mendeleyev (Bibl.1). In studying the oscillations of balances, this famous chemist found that their damping depended on the nature of the support on which the knife-edge of the beam rests.

To study this phenomenon, Mendeleyev designed two pendulums, one in the shape of a horseshoe with a setscrew and the other in the form of a slotted ring with a prismatic support. In 1898, he suggested to use this simple and accurate method for testing the hardness and for comparing the qualities of metals and alloys, woods, stones, glass, etc.

Various authors picked up this idea, some of whom such as Le Rolland, Herbert, Walker, Popoff (Bibl.2, 3, 4, 5) were more concerned with the variations of the period while others such as Kuznetsov, Rehbinder, König, Yakubovich and Persoz (Bibl.6, 7, 8, 9, 10) attached more importance to the rate of amplitude decay.

The characteristics of such a pendulum were standardized for the testing

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* Numbers in the margin indicate pagination in the original foreign text.

of paints in France in 1948 (Bibl.11) and are just about to be standardized (but with different values) in Germany (Bibl.12). Various laboratories have adopted this method for studying the drying of paints or their setting as a

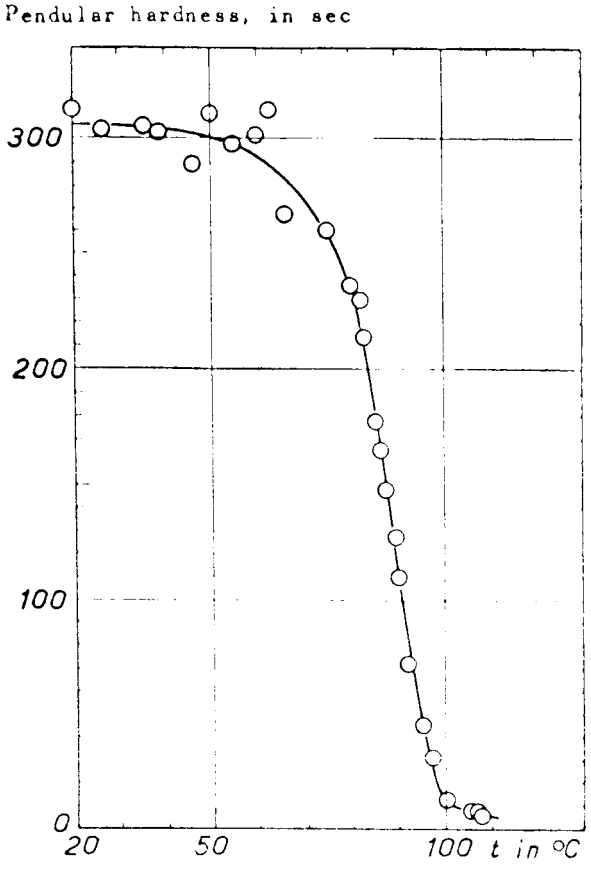

Fig.1 Pendulum Hardness of Polystyrene P3 as a Function of the Temperature

function of the time of cooking and specifically to determine a "pendular hardness" for varnishes, paints, and plastic materials. /12

For metals and alloys, this standardized model is not quite as suitable. In these cases, the pendulum would have to be ten times as heavy and would have to rest on the specimen on smaller balls.

According to the French Standard, the two balls have a diameter of 8 mm while the mass is 500 gm, the period is one second, and the center of gravity is 6 cm above the surface to be studied. The "pendular hardness" is conventionally taken as the time required by the amplitude to decrease from 12° to 4°. This particular instrument has been used in the work reported here.

II. GLASS-RUBBER TRANSITION

At low temperatures, high polymers even the types without crosslinking are hard and brittle. Their Young's modulus is of the order of 3×10^9 Pa (i.e., 3×10^{10} bars or 300 kgp/mm^2). Above a certain temperature, which varies from one polymer to the other, the thermal agitation is sufficient for causing the relatively long molecular fractions to diverge so that the material becomes much more deformable. This represents the rubber-like state, which corresponds to a Young's modulus of the order of 10^6 Pa (i.e., 10^7 bars or 100 gp/mm^2).

The transition between these two states extends over several tens of degrees so that it should be of interest to define, more or less arbitrarily, a more accurate transition temperature.

II.1. Definition of T_i

A preliminary definition is based on the variations of the modulus.

The modulus measured in the vitreous state (E_1) and in the elastomer state (E_2) varies relatively little with the time of application of the stress and with the temperature. Conversely, in the transition zone this modulus depends extensively on these factors. The time is fixed arbitrarily at 10 sec. The curve of the modulus, measured 10 sec after an abrupt elongation which then was maintained constant, is plotted as a function of the temperature. The temperature T_i (inflection) is the temperature for which the measured modulus reaches a value of $\sqrt{E_1 E_2}$. It is obvious that a time other than 10 sec would yield a different value for T_i.

II.2. Definition of T_g

The conventional definition is based on dilatometric studies that demonstrated a discontinuity of the cubic dilatation coefficient at a temperature denoted by T_g. Unfortunately, the position of this discontinuity depends on the velocity with which it is traversed. In addition, this method cannot be readily applied to methyl polymethacrylate which liberates monomer on heating.

III. EXPERIMENTAL PROCEDURE

We have attempted to define the transition point by an extremely simple mechanical process, using the decrease in pendular hardness with temperature.

The hardness-testing pendulum and its support are placed in a thermostatic cage made of Isorel and measuring about 50 × 50 × 70 cm, heated by two infrared 250-w bulbs installed near the bottom and illuminating the lower portion of the oven. A contact thermometer, whose cistern is placed in the immediate vicinity of the specimen, is used for controlling its temperature.

After the oven had been kept at the required temperature for several hours, the specimen is rapidly placed on the support and the measurement itself is made 30 min later.

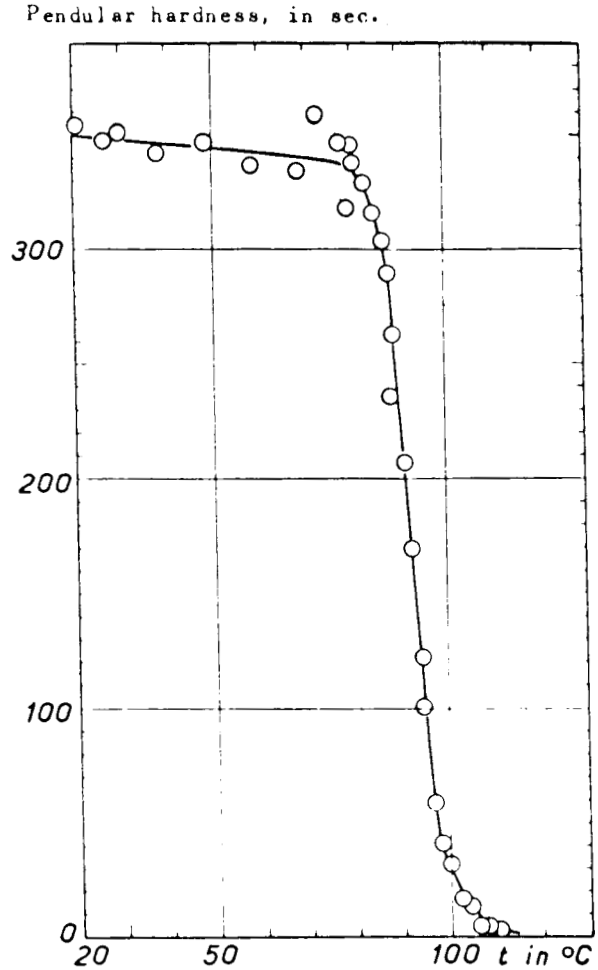

Fig.2 Pendular Hardness of Polystyrene C 100, as a Function of the Temperature

As always in such a case, the plastic material works in heat, its hardness increasing with the time of residence in the oven. For this reason, a time of $\frac{1}{2}$ hour was selected and each individual specimen was used only once.

IV. RESULTS

The pendular hardness was determined at various temperatures for four plastic materials:

1) Polystyrene P 3 manufactured by the B.A.S.F.(Bad.Aniline & Soda Fabr.) and extruded in sheets of 1 mm thickness in a plant of the Kodak Co.;

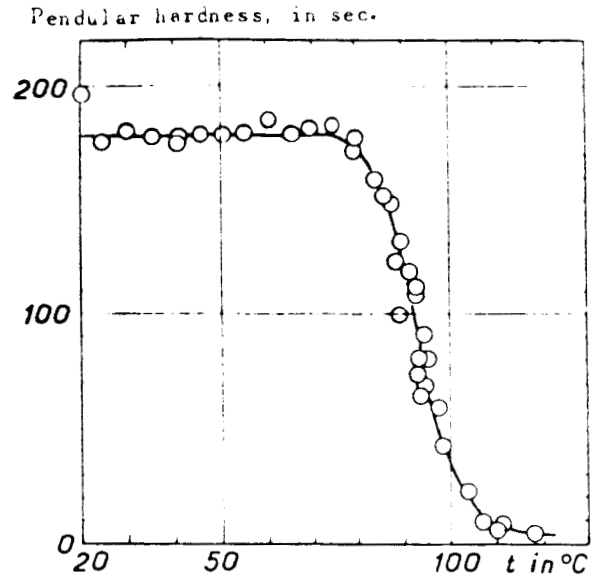

Fig.3 Pendular Hardness of Plexiglas M 33 as a Function of the Temperature

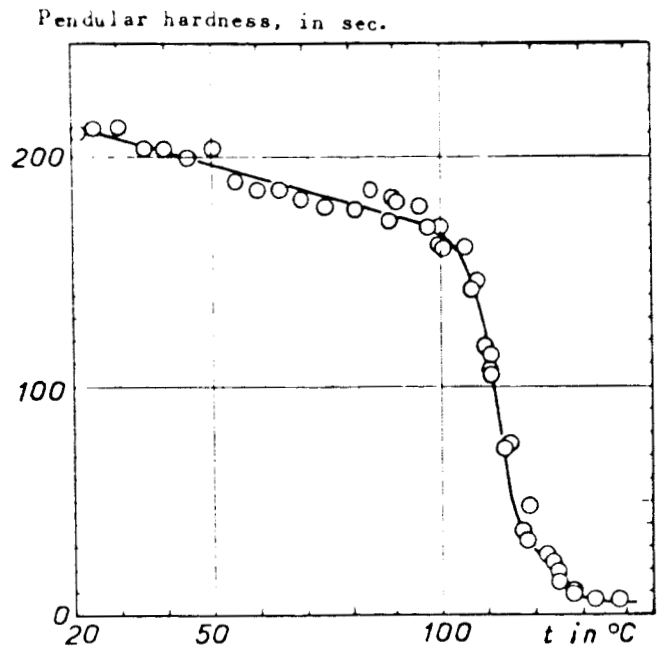

Fig.4 Pendular Hardness of Oroglas as a Function of the Temperature

2) Polystyrene C 100 manufactured by the Péchiney-Saint-Gobain Co., molded in small sheets of 1 × 8 × 10 cm by the same Company;

3) Plexiglas M 33, manufactured by the Alsthom Co.;

4) Oroglas 55, aircraft quality, manufactured by Rohm & Haas Co.

The experimental results are graphically presented (Figs.1 - 4) and the reference points obtained from the mean curves for rounded-off temperatures are compiled in Table I. /13

V. TRANSITION POINT T_p

The abrupt drop in hardness at the transition point led us to define a temperature T_p for the inflection point of the curve; however, for greater accuracy it is preferable to use here the temperature at which the hardness is

TABLE I

Temperature (°C)	Pendular hardness (sec)			
	Polystyrene P 3	Polystyrene C 100	Plexiglas M 33	Oroglas 55
20	305	350	178	213
30	304	348	178	208
40	302	346	178	203
50	299	344	178	197
60	292	342	178	191
70	273	340	178	186
80	234	336	173	180
85	182	317	157	177
90	110	235	122	175
95	44	110	66	172
100	12	31	38	167
105	8	11	17	154
110		3	7	123
115			5	62
120			4	30
125				16
130				8
135				6
Value of T_p in °C	87.5	92.5	92.8	112.3

half that of the vitreous state. To take account of cases in which the hardness of the vitreous state itself varies with the temperature (case of Oroglas 55), we are suggesting the following definition: T_p represents the tem-

perature at which the hardness has dropped to half of the value it had at T_p - - 50°C. Determined in this manner, the transition temperatures are shown in /14 Table I.

VI. COMPARISON WITH OTHER DATA FOR THE SAME MATERIALS

VI.1. Value of T_g for Polystyrenes

The two polystyrenes used here as a typical example were tested by the dilatometric method (Sec.II.2) by Braun, in Strasbourg, for times of the order of 0.01 hour. The resultant values for T_g were as follows:

Polystyrene P 3: 87°C
Polystyrene C 100: 96°C.

VI.2. Data Obtained by Measuring the Birefringence

Polystyrene P 3, Plexiglas M 33, and Oroglas 55 were tested at various temperatures under elongation at constant load*. In each case, the birefringence was measured one minute after application of the load. It should be mentioned, incidentally, that the double refraction, for the same time and the same temperature, is not proportional to the stress. However, for low stresses, the proportionality is sufficient for defining a Brewster coefficient, which was used for plotting the curves in Figs.5, 6, and 7.

VI.2.1. Polystyrene P 3

The first of these diagrams refers to Polystyrene P 3. In the vitreous domain, the Brewster coefficient, which is positive immediately after load application, diminishes with time and then changes to negative.

At 30°C, this change in sign takes place after a period of 4 months and 10 days:
At 50°C, the change takes place after 11 days and 8 hours;
At 60°C, after 37 hours;
At 70°C, after 7 hours;
At 80°C, after 6 min;
At 82.4°C, after 1 min.

An increase in stress, incidentally, diminishes this inversion time.

Consequently, at 82.4°C the curve in Fig.5 intersects the abscissa. It is obvious that, if a shorter time had been selected, the intersection temperature

* Polystyrene C 100, because of its residual birefringence produced by the molding process, has not been studied from this viewpoint.

would have been slightly higher.

Beyond the temperature of glass transition, the Brewster coefficient appears as negative as soon as it is materially possible to measure it, i.e., a few seconds after application of the load.

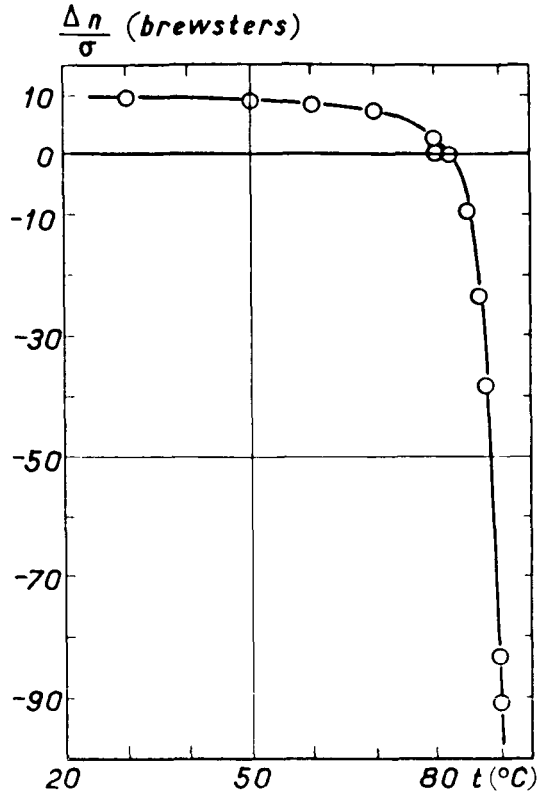

Fig.5 Brewster Coefficient of Polystyrene P 3,
One Minute after Application of the Stress

Consequently, one would be tempted to say that the inversion time becomes zero at the glass transition time, but ordinary caution makes it preferable to have this hypothesis verified by a high-speed instrument.

VI.2.2. Plexiglas M 33 and Oroglas 55

This phenomenon, however, is particular to polystyrene. For acrylic resins, the development of the Brewster coefficient with time and with temperature is entirely different (Figs.6 and 7). No change in sign occurs at constant temperature and constant stress. In the vitreous domain, this coefficient is negative from the moment of application of load and increases in absolute value with time. Its value, measured one minute after application of the load, becomes

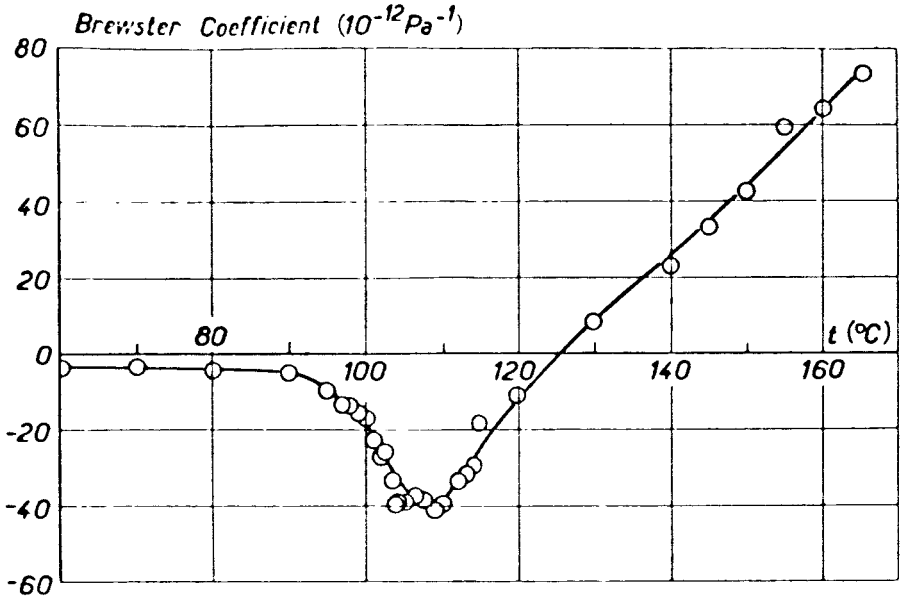

Fig.6 Brewster Coefficient of Plexiglas M 33, One Minute after Application of the Stress

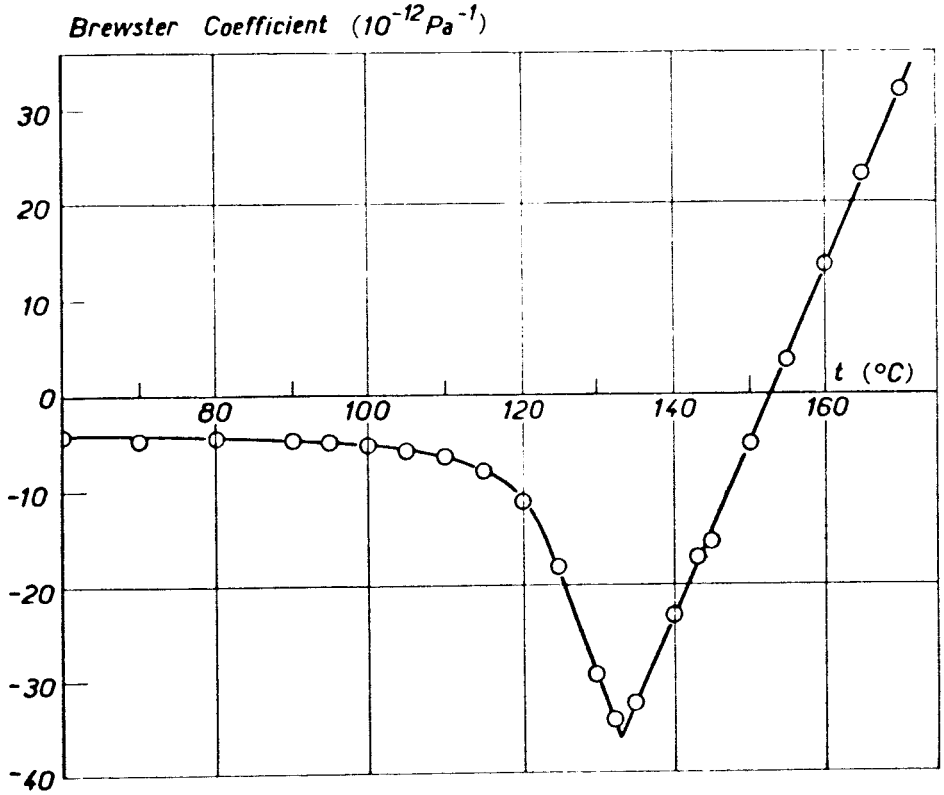

Fig.7 Brewster Coefficient of Oroglas 55, One Minute after Application of the Stress

increasingly negative as the temperature increases and then passes through a discontinuity point and thereafter reverses again to positive while increasing rapidly and almost linearly with the temperature. Two characteristic temperatures can be obtained from these curves: the temperature of the discontinuity point and the temperature of inversion. The values are as follows:

	Discontinuity Point	Inversion Point
Plexiglas M 33	109°C	126°C
Oroglas 55	133°C	153°C

This means that both are located in the elastomer domain.

VII. CONCLUSIONS

We have proposed here a simple and low-cost device, suitable for determining the glass transition temperature to within a few degrees. The tests were made on four resins, two polystyrenes, and two commercial polyacrylics. The obtained results for the two first materials practically coincide with the dilatometric tests run by the Strasbourg Macromolecular Research Center, but the dilatometric method is not as convenient for the other two materials because of the fact that they liberate monomers at elevated temperature.

Parallel to these hardness tests, we also studied the variation in mechanical birefringence of three of these resins with the temperature, in the hope of correlating the specific data with the transition point.

For polystyrene, the time required by the Brewster coefficient to change its sign after application of the stress apparently becomes zero or at least extremely small in the vicinity of the transition point.

For the various types of Plexiglas, the discontinuity point in the Brewster-coefficient curve versus temperature, is located at 16.2° and 20.7°C above the transition point and therefore cannot be identified with the latter.

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